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OPTICALLY TRANSPARENT CERAMICS BASED ON YTTRIUM OXIDE USING CARBONATE AND ALKOXY PRECURSORS

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Methods for producing optically transparent ceramic materials based on Y_2O_3 using carbonate and alkoxy precursors are considered. It is established that ceramic synthesized from yttrium isopropylate has better optical parameters than ceramics based on yttrium carbonate under equal heat treatment and firing regimes.

Progress in science and engineering is closely related to the development of new inorganic materials that have special optical properties. In the past 15 – 20 years numerous studies have been carried out in the field of transparent ceramics, which finds wide application in various sectors of engineering. Such ceramics were initially developed on the basis of aluminum and yttrium [1].

The upgrade in producing ceramics from pure oxides, the advance in the theory of sintering, and the progress in high-temperature technologies have opened possibilities for synthesizing transparent polycrystalline materials that in some physical properties surpass glass and single clear crystals.

While the optical characteristics of transparent ceramic materials are close to those of monocrystals, the advantages of ceramics are a lower production cost, the possibility of producing articles of complex shapes, and higher thermal resistance and strength; at the same time ceramics surpass glass in thermal conductivity, heat resistance, and hardness [2].

The purpose of our study is to obtain optically transparent ceramics based on Y_2O_3 activated by Nd^{3+} crystals with a HfO_2 additive facilitating sintering and with carbonate and alkoxy precursors.

In order to obtain transparent ceramics, it is necessary to decrease diffusion mass transfer between the crystals in order to lower the probability of capturing pores during their growth, which is usually observed inside strong aggregates [1]. When hafnium oxide is introduced, cation vacancies are formed in the inner parts of the crystal, which facilitates diffusion mass transfer and perfects the structure inside the crystal:

$$3HfO_2 \xrightarrow{Y_2O_3} 3Hf'_Y + 6O_O^x + V'''_Y . \qquad (1)$$
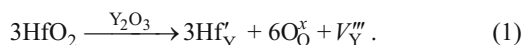
The segregation of hafnium oxide at the crystal boundaries leads to the formation of oxygen vacancies in the material (mainly the solid solution of Y_2O_3 in HfO_2), which impedes mass transfer between the crystals and facilitates their rapid growth and the capture of intercrystalline pores:

$$Y_2O_3 \xrightarrow{HfO_2} 2Y'_{Hf} + 3O_O^x + V''_O . \qquad (2)$$
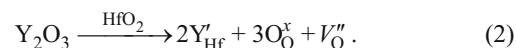
Based on published data [3], the following composition was used in our study (mol.%): 93 Y_2O_3, 6 HfO_2, and 1 Nd_2O_3.

The main batch components included: industrial yttrium carbonate, whose content of rare-earth oxides and impurities meets standard TU-48-4-191–72; yttrium carbonate synthesized by pulverizing a highly concentrated yttrium chloride solution into a cold solution of ammonium carbonate acting as the precipitator [4]; yttrium isopropylate produced in an exchange reaction of anhydrous yttrium chloride with metallic sodium in the medium of isopropyl alcohol [5].

Industrial yttrium carbonate contains particles of size 3 – 5 μm; 30% of these particles have a size up to 30 μm. Yttrium carbonate produced by precipitation from highly concentrated solutions contains particles of size below 1 μm joined in loose amorphous aggregates of size 10 – 30 μm.

The consolidating additive of hafnium oxide was introduced into the batch in the form of hafnium oxynitrate and the neodymium oxide additive in the form of neodymium nitrate [6].

Analysis of thermograms has established that complete decomposition of all salts making part of the batch ends at 700°C, which provides optimum conditions for the formation of solid solutions.

The milling of components is performed by the moist method in a planetary mill for 5 min using milling bodies made of yttrium oxide. The milling of initial yttrium carbonate powder was performed in an aqueous solution of the additive salts, which was prepared to achieve a preset concentration of hafnium and neodymium oxides in hot distilled

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water acidified to pH = 2 – 4. This solution provided for complete dissolution of the additive salts and pickling of the surface of the carbonate particles, which facilitated the disintegration of strong aggregates.

The suspension obtained after milling was dried at a temperature of 150°C. The powder was grated through a nylon sieve with a cell size of 63 μm and then calcined in a Silit furnace at a temperature of 1400°C.

The microscopy study of calcined powders demonstrated that the type of initial material has a significant effect on the shape and size of yttrium oxide particles. Thus, the powder obtained from the industrial carbonate consists of irregular-shape particles of size 1 – 3 μm. Yttrium oxide powder based on the synthesized carbonate is represented by spherical particles of size 200 – 300 nm joined in loose aggregates of a size not more than 1 μm.

The solution of yttrium isopropylate in isopropanol was poured into a conic flat-bottom flask, then distilled water was quickly added to it under intense stirring. A semitransparent viscous gel was formed. At the end of the hydrolysis this gel was rinsed with distilled water to remove the byproducts, in particular NaOH formed in the hydrolysis of yttrium isopropylate.

Differential thermal analysis of the products of hydrolysis of yttrium isopropylate without additives established that its decomposition proceeds in two stages. The hydrolyzate is presumably a compound of the type $Y(OH)_x(OR)_{3-x}$ ($x = 1 – 3$), i.e., the oxyisopropyl groups in hydrolysis of the alcoholate may be incompletely replaced by OH^- groups.

At the first stage at 100 – 200°C solvate water is presumably removed from the hydrolysis product and at 300 – 400°C part of the OH^- groups are split off and a YOOH compound is formed, which at 600 transforms into Y_2O_3.

The obtained residue was mixed with 5% aqueous PVA solution so that its amount is equal to 10% of the solid phase weight (converted to yttrium oxide); then the required quantity of hafnium and neodymium was introduced. After that the gel was mixed for 30 min for a uniform distribution of the PVA between the particles and sorption on their surfaces. Then the gel was dried at 150°C for complete removal of moisture.

Microscopic analysis indicated that xerogel consists of lamellar particles of size 20 – 30 μm.

Xerogel was calcined in a Silit furnace at a temperature of 1400°C with 2-h exposure. In accordance with reactions (1) and (2), the structure inside the crystals was perfected, but large and strong aggregates were not formed.

A microscopic study of the synthesized powder established that it consists of rounded particles of size below 200 nm, which are joined in loose secondary aggregates of size 1 – 2 μm.

The solution of 5% PVA in the amount of 15% was introduced into the powder obtained and grated through a sieve with 63 μm cell size; then the samples were molded.

Samples of diameter 22 and thickness 2.5 – 3.0 mm were molded by semidry molding at a pressure of 100 MPa. The preforms were fired in air at 1400°C with exposure for 2 h at the final temperature, then in vacuum (10^{-6} mm Hg) in the temperature interval of 1750 – 1950°C for 2 h. Next, oxidizing firing was carried out in air with 2 h exposure and the refining firing in vacuum at 700°C with 30-min exposure at the final temperature.

The properties of the samples based on different types of materials are shown in Table 1. To increase light transmission and relative density, we performed firing with an intermediate exposure for 30 min at 1500°C. The results are listed in Table 1 as well.

It follows from the data that regimes with an intermediate exposure make it possible to raise the relative density of ceramics based on yttrium isopropylate from 99.5 to 99.7 %, the crystal size from 8 to 12 μm, and the light transmission in the visible spectrum range from 43 to 48%.

Carbonate-based materials actually do not exhibit increments in relative density; their crystal sizes and light transmission remain the same as without the intermediate exposure. The poorer transparency and relative density parameters are related to the presence of stronger and larger aggregates in the mixture.

Raising the firing temperatures to 1810°C makes it possible to raise the relative density of ceramics based on isopropylate to 99.9%; the crystal size in this case grows to 15 – 20 μm. Petrographic analysis indicates that the habitus of these crystals is isometric; two types of solid solutions are clearly identified: HfO_2 in Y_2O_3 and Nd_3O_3 in Y_2O_3.

The decrease in the relative density of the carbonate-based sintered samples (Table 1) is presumably due to the fact that their porosity does not have time to disappear from the relatively strong porous aggregates and the pores become captured by the rapidly growing crystals. This may be facilitated by the capture of carbon in its oxide form by Y_2O_3 crystals. Carbon dioxide being more acid presumably displaces hafnium oxide at the crystal boundaries. At high temperatures CO_2 starts evaporating with the simultaneous disappearance of oxygen vacancies which impede mass transfer between the crystals, their rapid growth, and the capture of intercrystalline pores (reaction (2)). In these conditions recrystallization leads to the capture of the pores and decreases transparency.

A similar phenomenon is observed in producing transparent ceramics based on Al_2O_3 with additives of magnesium, yttrium, or lanthanum oxides. Whereas the introduction of MgO facilitates the formation of oxygen vacancies, carbon dioxide counterbalances the effect of magnesium oxide and thus decreases the concentration of oxygen vacancies [7].

$$MgO \xrightarrow{Al_2O_3} Mg'_{Al} + O_O^x + V_O'' ;$$

$$MgO + CO_2 \xrightarrow{Al_2O_3} Mg'_{Al} + C'_{Al} + 3O_O^x .$$

TABLE 1
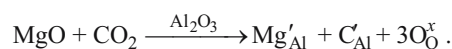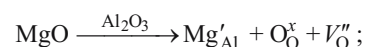
Initial material	Firing temperature, °C	Microstructure characteristics			Sealed porosity		Light transmission, %	Relative density, %
		phase	habitus	particle size, μm	size, μm	quantity, %		
Without intermediate exposure								
$Y_2(CO_3)_3$	1750	Y_2O_3 Solid solution:	Isometric	8	5	0.2	18	98.7
		HfO_2 in Y_2O_3	The same	1 – 2				
		Nd_2O_3 in Y_2O_3	Prismatic	6 – 8				
Y(*i*-PrO)$_3$	1750	Y_2O_3 Solid solution:	Isometric	8	–	–	42	99.5
		HfO_2 in Y_2O_3	The same	3				
		Nd_2O_3 in Y_2O_3	″	3				
With intermediate exposure for 30 min at 1500°C								
$Y_2(CO_3)_3$	1750	Y_2O_3 Solid solution:	Isometric	5 – 12	4	0.1	19	99.8
		HfO_2 in Y_2O_3	The same	1 – 2				
		Nd_2O_3 in Y_2O_3	Prismatic	4 – 5				
Y(*i*-PrO)$_3$	1750	Y_2O_3 Solid solution:	Isometric	8 – 12	–	–	48	99.7
		HfO_2 in Y_2O_3	The same	1				
		Nd_2O_3 in Y_2O_3	″	2 – 3				
$Y_2(CO_3)_3$	1810	Y_2O_3 Solid solution:	″	12 – 24	8	0.1	15	98.7
		HfO_2 in Y_2O_3	″	3				
		Nd_2O_3 in Y_2O_3	″	2				
Y(*i*-PrO)$_3$	1810	Y_2O_3 Solid solution:	″	15 – 20	–	–	64	99.9
		HfO_2 in Y_2O_3	″	2				
		Nd_2O_3 in Y_2O_3	Prismatic	4 – 6				

A further increase in temperature up to 1950°C lowers the relative density of Y_2O samples to 96 – 98%, decreases the linear shrinkage to 16 – 17%, and causes a complete loss of transparency and a significant growth of the crystal sizes. It should be noted that not all samples based on the industrial carbonate are opaque with visible inclusions. This is another confirmation of the effect of the prehistory of yttrium oxide on the optical properties of ceramics.

Thus, ceramics based on industrial yttrium carbonate has poorer properties than the material based on yttrium carbonate synthesized in the laboratory conditions. The powders obtained by hydrolysis of yttrium isopropylate have smaller particles. They have been used to produce optically transparent ceramics with light transmission in the visible spectrum equal to 64%.

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